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Lamellar-in-Lamellar Structure of A-*b*-(B-*b*-C)$_m$-*b*-B-*b*-A Multiblock Copolymers

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ABSTRACT: The number k of "internal" layers for the lamellar self-assembled state of a new class of multiblock copolymers A-*b*-(B-*b*-C)$_m$-*b*-B-*b*-A is determined as a function of m in the strong segregation limit. Here the outer A-blocks are assumed to be considerably longer than the $m + 1$ blocks of equal length of the (B-*b*-C)$_m$-*b*-B middle multiblock, and the self-assembled state is assumed to consist of k "thin" B- and C-layers sandwiched between "thick" A-layers. The predictions are in excellent agreement with the available experimental data.

Introduction

Hierarchically ordered block copolymer-based systems have become an active area of research recently.[1−21] Such systems are characterized by the formation of structures involving different length scales. In most cases diblock copolymers are involved where one of the blocks contains side groups that either are fully flexible or contain mesogenic units. Furthermore, the side groups can be covalently linked or attached via physical interactions such as, e.g., hydrogen bonding. Here the diblock nature of the molecules represents one of the length scales while the other is associated with the side groups and thus with the graftlike nature of one of the blocks. More recently, linear multiblock copolymers with two different intrinsic length scales have been introduced.[5,16−20] In this paper we consider the simplest representative of this class of systems consisting of a A-*b*-(B-*b*-C)$_m$-*b*-B-*b*-A multiblock copolymers. It is assumed that the A-blocks contain N segments, whereas the B- and C-block each consists of the same number of n segments with $n \ll N$. We will consider the situation where B- and C-layers are formed in between A-layers. Furthermore, strong segregation with respect to all chemically different species involved will be assumed. This case corresponds to the experimental P2VP-*b*-[(PI-*b*-PS)$_4$-*b*-PI]-*b*-P2VP multiblock copolymer system investigated by Matsushita and co-workers.[19] Here PI is polyisoprene, P2VP is poly(2-vinylpyridine), and PS denotes polystyrene. They found that the middle (PI-*b*-PS)$_4$-*b*-PI multiblock formed five layers (alternately PI and PS) in between successive P2VP layers (see Figure 1). In ref 19 a combinatorial argument was presented to explain the number of internal layers.

Here we will address this problem of the number k of internal B- and C-layers for self-assembled A-*b*-(B-*b*-C)$_m$-*b*-B-*b*-A multiblock copolymers as a function of the pertinent parameters, notably m, in more detail.

Results and Discussion

The number k of internal B- and C-layers for self-assembled A-*b*-(B-*b*-C)$_m$-*b*-B-*b*-A multiblock copolymers as a function of the pertinent parameters, notably m, equals $k = 3$, 5, 7, ..., and

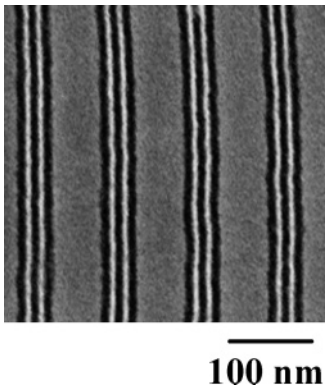

Figure 1. Lamellar-in-lamellar self-assembled state of P2VP-*b*-[(PI-*b*-PS)$_4$-*b*-PI]-*b*-P2VP multiblock copolymer system (courtesy Prof. Yushu Matsushita).

the precise value should be obtained from a free energy minimization. To address this, we will make the simplifying assumption that the statistical segment length and the volume per segment are identical for all species involved. They will be denoted as a and v. The global multiblock conformation can be either a bridge, which starts from one A-layer and ends in the next A-layer, or a loop, which starts and ends in the same A-layer. Both the multiblock bridge and the multiblock loop consist of a sequence of local loops and bridges and A-tails, as illustrated in Figure 2.

If x is the fraction of multiblock bridges and $1 - x$ the fraction of multiblock loops, then the average energy per copolymer chain is given by

$$F = xF_{\text{bridge}} + (1 - x)F_{\text{loop}} + x \ln x + (1 - x) \ln (1 - x) \quad (1)$$

where F_{bridge} is the bridge free energy and F_{loop} is the loop energy. Using a mean-field picture and assuming that the average number of local loops and bridges in the global loop conformation is approximately equal to the average number of local loops and bridges in the global bridge conformation, in as a first approximation we will assume that $F_{\text{bridge}} = F_{\text{loop}}$ and $x = {}^1/_2$. Hence, $F = F_{\text{bridge}} - \ln 2$.

Next we concentrate on the multiblock bridge conformation which consists of a sequence of local loops and bridges. Because

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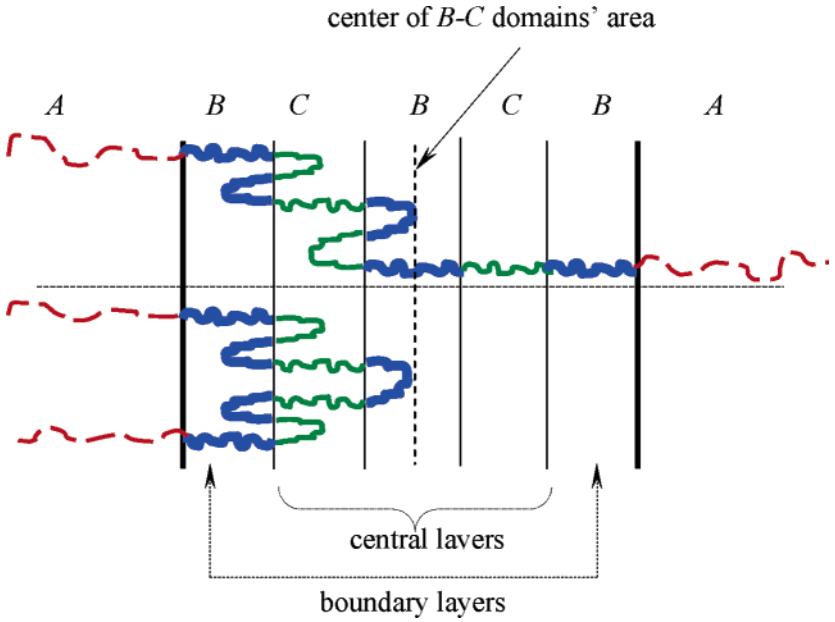

Figure 2. Schematic representation of a global bridge and a loop A-*b*-(B-*b*-C)$_m$-*b*-B-*b*-A ($m = 4$) multiblock copolymer conformation.

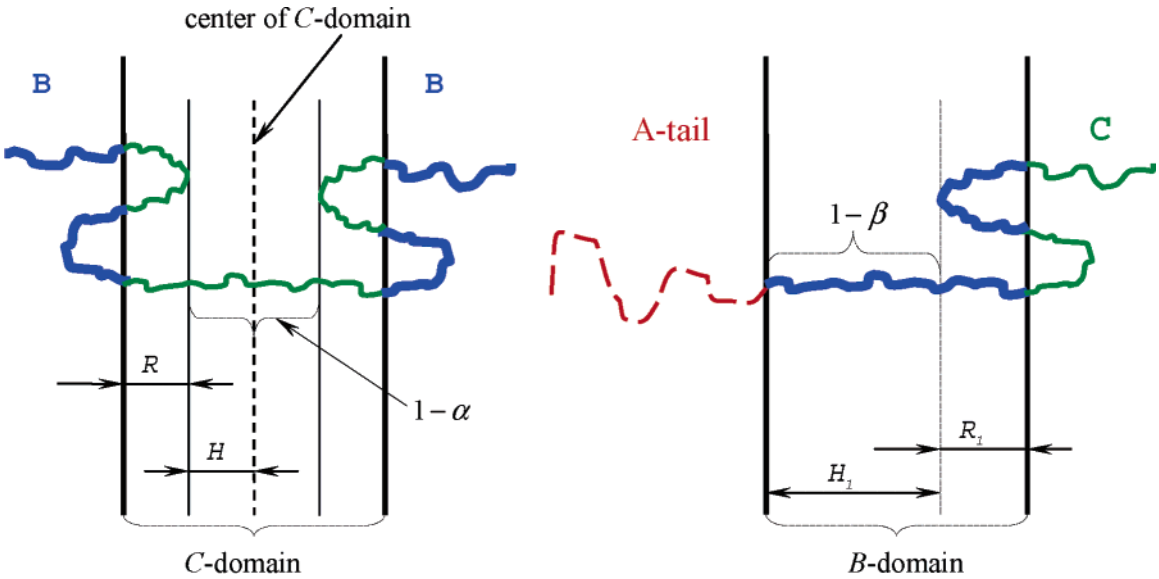

Figure 3. Left: schematic representation of multiblock copolymer conformation in the C-layer. The loops are repelled from the center of the domain. R denotes the thickness of the loop region, and $2H$ is the thickness of the middle part of the C-layer where only bridging chain segments are present, $1 - \alpha$ being the fraction of the bridging segments that are in the $2H$ region. Note that in the $2H$ region the bridging chains are uniformly stretched whereas they are nonuniformly stretched in the region where both loops and bridges are present. Right: schematic representation of multiblock copolymer conformation in the B-layer adjacent to the A-layer. R_1 denotes the thickness of the loop region, and H_1 is the thickness of the middle part of the C-domain where only segments belonging to the bridging chain are present, $1 - \beta$ being the fraction of the bridge segments in the H_1 region.

Table 1. Number of Internal Layers *k*

predictions of ref 19		predictions of present model	
m	*k*	*m*	*k*
2	3	2	3
3	5	3	5
4	5	4	5
5	5	5	7
6	5	6	7
7	7	7	9

of the assumed strong incompatibility between the A- and C-blocks, we expect that the multiblock forms only one bridge in the first B-layer located in between the A- and C-layers. The number of bridges in the central B- and C-layers depends on two factors, namely on the degree of stretching of the multiblock and the thermal fluctuations. For strong multiblock stretching the thermal fluctuations are small, and only one bridge per domain is formed. We will focus on this case because this also seems to be the situation realized in recent experiments.[19] Besides the first and last B-block, the remaining $(2m - 1)$ blocks connecting the two boundary B-layers span $(k - 2)$ layers. Therefore, the probability p that a block is a bridge equals

$$p = \frac{k - 2}{2m - 1} \tag{2}$$

The $(2m - 1)$-block chain consists of $(k - 2)$ parts which we will call blobs. Each blob contains on average $(2m - 1)/(k - 2)$ blocks including one bridge and loops. The chain of blobs

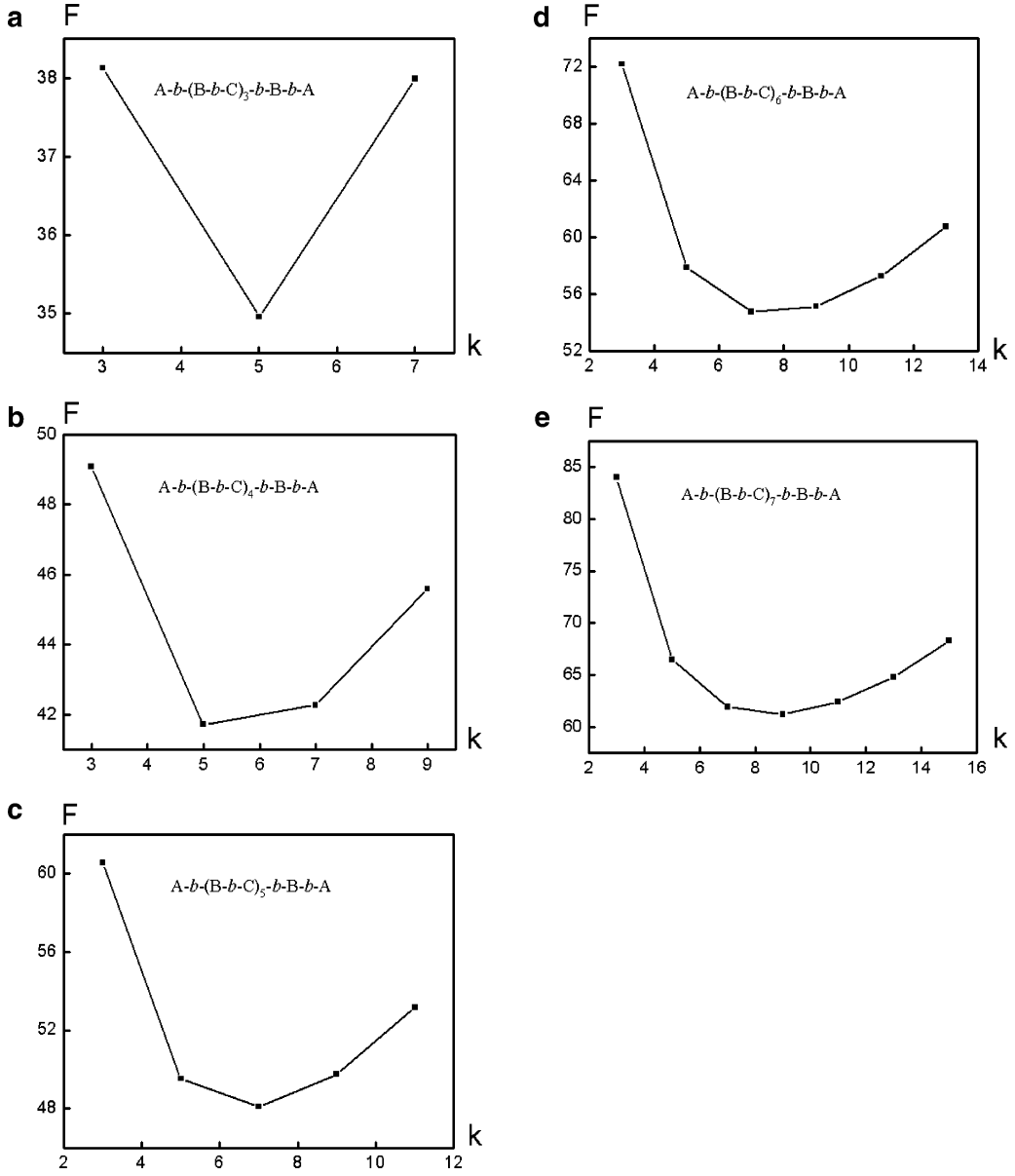

Figure 4. Free energy F of the A-*b*-(B-b-C)$_m$-*b*-B-*b*-A multiblock copolymer as a function of the number k of internal layers for $\chi_{AB}N = 340$, $\chi_{BC}/\chi_{AB} = 0.25$, and $n/N = 0.2$: (a) $m = 3$, (b) $m = 4$, (c) $m = 5$, (d) $m = 6$, and (e) $m = 7$. The values of k at the minima of $F(k)$ are given in Table 1.

is stretched in one direction; therefore, the probability of this conformation is $(1/2)^{k-2}$. It corresponds to a conformational free energy (in units k_BT) $F_{conf} = (k - 2)$ ln 2. The total free energy per multiblock copolymer includes the AB interfacial free energy F_{AB}, the BC interfacial free energy F_{BC}, the elastic free energy of the A-domain F_A, the elastic free energy of the two boundary B-layers that are in contact with the A-layers $F_{B,1}$, the elastic free energy $F_{B,2}$ and F_C of the central B- and C-layers, and the conformational free energy of the multiblock copolymer chain:

$$F_{bridge} = 2F_{AB} + (k-1)F_{BC} + F_A + 2F_{B,1} + \frac{k-3}{2}F_{B,2} + \frac{k-1}{2}F_C + F_{conf} \quad (3)$$

The interfacial free energies depend on the corresponding interfacial tension and average area per multiblock copolymer Σ

$$F_{AB} = \gamma_{AB}\Sigma \qquad F_{AB} = \gamma_{BC}\Sigma \quad (4)$$

where $\gamma_{AB} = (a/v)(\chi_{AB}/6)^{1/2}$, $\gamma_{BC} = (a/v)(\chi_{BC}/6)^{1/2}$, and χ_{AB}, χ_{BC} are the Flory−Huggins parameters. The elastic free energy of the A-layer is given by[22]

$$F_A = \frac{\pi^2 N v^2}{4a^2\Sigma^2} \quad (5)$$

For the calculation of the elastic free energy of the B- and C-layers we use the method that has been presented in refs 23 and 24. Since the free energy of the central B- and C-layers are the same, $F_{B,2} = F_C$, we consider the C-layer only. A C-layer consists of one bridge and loops (Figure 3a). The loops are repelled from the middle part of the domain and occupy a layer of thickness R. The total thickness of the C-layer is $2(R + H)$, and the middle section of thickness $2H$ is occupied by bridge segments only. If we denote the fraction of bridge segments in the middle layer as $1 - \alpha$, then the equilibrium condition implies that

$$H = \frac{\pi}{2}R(1-\alpha)\cot\left(\frac{\pi\alpha}{2}\right) \quad (6)$$

and the probability of a bridge is given by eq 7, determining α

$$p = \frac{\pi}{\pi(1-\alpha) + 2\tan\left(\frac{\pi\alpha}{2}\right)} = \frac{k-2}{2m-1} \tag{7}$$

The elastic free energy of the multiblock per central domain involves on average Q-blocks, one of which is a bridge and the others are loops, and is given by

$$F_{B,2} = F_C = \frac{6QpH^2}{a^2 n(1-\alpha)} + \frac{3\pi QpR^2}{a^2 n}\cot\left(\frac{\pi\alpha}{2}\right) + \frac{\pi^2\Sigma R^3}{a^2 n^2 \upsilon} \tag{8}$$

Similarly, we can consider the boundary B-layer (Figure 3, bottom). Let R_1 be the thickness of the section containing loop and bridge segments, and the remaining part of thickness H_1 is occupied by bridge segments only. If β is the fraction of the bridge segments belonging to the layer of thickness R_1,then

$$R_1 = \frac{n\upsilon}{\pi\Sigma}\tan(\pi\beta), \quad H_1 = \frac{n\upsilon(1-\beta)}{\Sigma} \tag{9}$$

and the elastic free energy of the boundary B-layer is given by

$$F_{B,1} = \frac{3n(1-\beta)\upsilon^2}{a^2\Sigma^2} + \frac{3\pi R_1^2}{a^2 n}\cot(\pi\beta) + \frac{\pi^2\Sigma R_1^3}{a^2 n^2 \upsilon} \tag{10}$$

Using the incompressibility condition, we can express Q and R as a function of α and β

$$Q = \frac{q(\beta)}{k-2}, \quad R = \frac{n\upsilon p(1-\alpha)q(\beta)}{2\Sigma(k-2)}$$

$$q(\beta) = 2m - 1 + 2\beta - \frac{2}{\pi}\tan(\pi\beta) \tag{11}$$

The average free energy per multiblock copolymer is thus given by

$$F = (k-3)\ln 2 + 2\gamma_{AB}\Sigma\left(1 + \frac{k-1}{2}\frac{\gamma_{BC}}{\gamma_{AB}}\right) + \frac{\pi^2 N\upsilon^2}{4a^2\Sigma^2}g(\alpha,\beta) \tag{12}$$

where

$$g(\alpha,\beta) = 1 + \frac{4}{\pi^2}\frac{n}{N}\left[f_1(\beta) + \frac{q^3p^3}{(k-2)^2}f_2(\alpha)\right] \tag{13}$$

with $f_1(\beta) = (\tan^3(\pi\beta))/\pi + (3\tan\pi\beta)/\pi + 3(1-\beta)$ and $f_2(\alpha) = \tan^3(\pi\alpha/2)/\pi + (3\tan(\pi\alpha/2)/\pi) + (3(1-\alpha))/2$. After minimization of the free energy with respect to Σ we get

$$F = (k-3)\ln 2 + 3\left(\frac{\pi}{2}\right)^{2/3}\left(\frac{\chi_{AB}N}{6}\right)^{1/3}\left(1 + \frac{k-1}{2}\sqrt{\frac{\chi_{BC}}{\chi_{AB}}}\right)^{2/3} g^{1/3}(\alpha,\beta) \tag{14}$$

In the limit of large m minimization of the last expression with respect to k gives as its asymptotic behavior

$$k \propto \begin{cases} 2m\left(\frac{n}{N}\right)^{1/3}, & 1 < m < \left(\frac{\chi_{BC}N^2}{n}\right)^{1/3} \\ \left(\frac{\pi}{2}\right)^{1/3}\left(\frac{m}{\ln 2}\right)^{1/2}\left(\frac{\chi_{BC}n}{6}\right)^{1/6}, & m > \left(\frac{\chi_{BC}N^2}{n}\right)^{1/3} \end{cases} \tag{15}$$

In the more realistic case of relatively small m the free energy should be considered as a function of odd values of $k = 3, 5, 7, \ldots$. The equilibrium value of k corresponds to the minimal value of $F(k)$. Explicit calculations have been performed for the situation that corresponds to the experimental system P2VP-*b*-[(PI-*b*-PS)$_m$-*b*-PI]-*b*-P2VP with $m = 4$ and for different values of $m = 3, 5, 6$, and 7. For the experimental system we have[19,25] $\chi_{AB}N = 340$, $\chi_{BC}/\chi_{AB} = 0.25$, and $n/N = 0.2$. The equilibrium values obtained for the number of internal layers k as a function of m are $k = 5, 5, 7, 7$, and 9, respectively. In Table 1 these are compared with the values given in ref 19 using combinatorial arguments only. The value of $k = 5$ found for $m = 4$ is exactly what has been observed experimentally. The corresponding plots of $F(k)$ are given in Figure 4a−e.

In summary, we see that, besides combinatorial contributions, i.e., the different ways of creating specific sequences of loops and bridges, the number of internal layers is determined to a large extent by the balance between the stretching of the individual blocks and the interfacial area. Of course, further efforts are required to calculate the conformational free energy more rigorously.

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